

APPENDIX B

SCIENTIFIC PEER REVIEW COMMENTS AND RESPONSES

Diazinon and Chlorpyrifos TMDL Upper Newport Bay and San Diego Creek (Draft of November 15, 2002)

Peer Reviewers:

(1) Ronald S. Tjeerdema, Ph.D., DABT, Professor of Environmental Toxicology,
University of California, Davis
January 10, 2003 letter to Wanda Smith

(2) Michael Stenstrom, Ph.D., P.E., Professor of Civil and Environmental Engineering,
University of California, Los Angeles
February 3, 2003 letter to Wanda Smith via email

Dr. Tjeerdema, General Comment:

In general, the document is well written and thorough. I like the approach of developing concentration-based, instead of mass-based, TMDLs for both insecticides. Also, as it is clear the use of both agents will be phased out for most applications over the next several years, this is considered a significant factor in attaining the targets for both San Diego Creek and Newport Bay. In general, the data used appear to be both reliable and their treatment here is generally defensible. Rationale is clearly stated, thus the report also supports its conclusions and recommendations. However, I do have several specific comments/recommendations, which are presented below.

For additional information on the environmental fate and toxic actions of diazinon, please refer to the following review:

Larkin, D. J. and R. S. Tjeerdema, 2000. Fate and Effects of Diazinon. *Reviews of Environmental Contamination and Toxicology* 166:49-82.

Dr. Tjeerdema, Specific Comments:

1. *Page 11. The reference LC50s for diazinon and chlorpyrifos in Ceriodaphnia, as reported by the California Department of Fish and Game (CDFG), are 440 and 60 ng/L, respectively. Since the numeric targets adopted for the TMDLs are based on the criteria derived by CDFG (please see pages 14 through 16), please provide a brief summary of how they were derived (using the referenced EPA guidelines). Also, please include the measured NOECs from the same CDFG tests. It is important to understand how the water quality criteria relate to the measured NOECs as well as the LC50s.*

Response: The *Ceriodaphnia* LC-50s were derived using seven acceptable tests for diazinon, and five acceptable tests for chlorpyrifos. Geometric means of the LC50s reported in these tests were calculated to derive the reported freshwater LC50s of 440 ng/L for diazinon and 60 ng/L for chlorpyrifos. Abstracts of these tests are available in the CDFG report (CDFG 200a). NOECs were not reported for most of the tests. For diazinon, the average acute NOEC for two of the *Ceriodaphnia* tests was 350 ng/L, while a chronic NOEC was reported as 220 ng/L. No acute NOECs were reported for chlorpyrifos, however a chronic NOEC of 29 ng/L was reported. This information has been incorporated into Table 3-1 of the TMDL report.

It should be emphasized that the recommended CDFG criteria were derived using toxicity data from eight families of aquatic animals. Acute toxicity values (LC50s and EC50s) were assembled from tests that met standard acceptance protocols defined in USEPA guidelines (1985) and ASTM standards. For diazinon, a total of 40 acceptable tests from 15 genera were used, and for chlorpyrifos a total of 33 acceptable tests from 18 genera were used. Genus mean acute values (GMAVs) were calculated using the geometric means of the reported acute values (LC50s or EC50s), and the four lowest GMAVs were used to calculate the acute criteria. Chronic criteria were derived using acute-to-chronic ratios. Thus *Ceriodaphnia* represented only one of the four genera used. This information has been included in Section 3.0 of the report.

2. *Page 18. Hydrolysis of diazinon is also considered a major dissipation pathway and, similar to chlorpyrifos, it is also pH dependent, as both slightly acidic and alkaline conditions enhance its degradation. Please refer to a pesticide reference text for more specific information to include in this section.*

Response: Additional text describing the hydrolysis dissipation pathway has been added to Section 4.1 as follows:

“For diazinon, major routes for dissipation are hydrolysis, biodegradation, volatilization, and photolysis (USEPA 1999a). Diazinon degrades rapidly by hydrolysis under acidic conditions (half-life of 12 days at pH 5). Hydrolysis is slower under neutral and alkaline conditions (abiotic hydrolysis half-lives of 138 days at pH 7, and 77 days at pH 9).”

3. Pages 18 and 19. Volatilization is cited as a major dissipation route for both insecticides (this is also discussed later in the draft), yet Table 4-1 lacks both vapor pressure (P) and Henry's law constant values (measured and/or calculated). Please add them, as they are readily available from reference texts and lend insight to the fate of both diazinon and chlorpyrifos.

Response: Table 4-1 has been updated to include the data requested:

Pesticide	<i>Ceriodaphnia</i> LC50 (ng/L)	Solubility (mg/L)	Adsorption Coefficient (dim'less)	Henry's Law (atm-mol/m ³)	Vapor Pressure (mmHg)	Half-Lives (days)	
						Soil	Water
Bifenthrin	78	0.1	1,000,000	n/a	n/a	7-240	n/a
Carbaryl	3,380	40	300	1.27×10^{-5}	4.1×10^{-5}	7-28	10
Chlorpyrifos	60	2	6070	4.16×10^{-6}	1.87×10^{-5}	60-120	30-75
Diazinon	440	40	1000	1.13×10^{-7}	8.47×10^{-5}	14-28	180
DDT	4,700	<1	100,000	n/a	n/a	2-15 years	20-60
Malathion	1,140	130	2.75	4.89×10^{-9}	1.25×10^{-6}	1-25	< 7

Sources: EXTOXNET Pesticide Information Profiles; CDFG (2000a); Montgomery (1993)
n/a=not available; dim'less=dimensionless

4. Pages 33 and 36. Atmospheric deposition is discussed as a source to the watershed of the two insecticides. In order to predict the magnitude of contribution, it is valuable to know the Henry's law constants, which can be used to estimate chemical partitioning between air-water interfaces. Please see my request in #3, above.

Response: Table 4-1 has been updated with the Henry's law data (see above)

Dr. Stenstrom, General Comments:

I am replying to your request for a review of the proposed TMDL for diazinon and chlorpyrifos in the Newport Bay Watershed. In your request you specifically asked me to consider if the data used in developing the report is reliable and defensible, and does the report as a whole support its scientific conclusions and recommendations. I conclude that it does, and I provide other comments later in this letter.

In the middle and later half of the 1990's, water quality toxicity was noted in many areas in California, and stormwater was suspected. Many toxicity studies were performed (some at UCLA in my laboratory). Gradually it became clear that the pesticides diazinon and chlorpyrifos were responsible. The draft TMDL documents several such studies for the Upper Newport Bay and San Diego Creek watersheds. Lee et al. conducted two studies with US EPA funding. The studies were specifically conducted to determine the existence of aquatic toxicity, and if possible, the source of the toxicity. The second study (final report dated May 2001) was successful in detected toxicity in the majority of the samples, including all stormwater samples. The "samples were highly toxic to Ceriodaphnia dubia and Mysidopsis bahia." They found no toxicity to fathead minnows or alga Selenastrum. They found approximately one-third to one-half of the toxicity to be from diazinon and/or chlorpyrifos. Diazinon and chlorpyrifos were implicated in specific samples to a much higher extent. I view this report as strong confirmation of what we suspected much earlier.

Contract laboratories performed the actual analyses. Aqua Science and UC Davis Aquatic Toxicology Lab. I reviewed the Aqua Science report and the UC Davis lab is known to me from other investigations. APPL Laboratories performed diazinon and chlorpyrifos analyses. I did not review their report, but I am familiar with analytical methods for these two pesticides. We perform pesticide analysis by GC and GC/MSD in my laboratory at UCLA. I am familiar with the Elisa procedures, although we do not perform this method in my laboratory. I regard it as a less expensive, quick method; it is useful but usually less precise than GC, HP/LC or GC/MSD methods. The differences between analytical methods noted in the Lee report do not surprise me, and they do not detract from the validity of the report's results or conclusions. Also, I do not believe a simple error such as inaccurate standards (as Lee suggests) is the reason the differences. It is more likely that the differences are due to matrix effects in the samples.

I would also like to note that attributing the source of the toxicity to diazinon and chlorpyrifos is a strong finding. It is much more common for toxicity studies to fail in their identification of toxicants, or to be able to identify them only by broad class (e.g., metals, oxidants, organic compounds, etc.).

It is my opinion that there is cogent, scientifically valid evidence that significant and frequent aquatic toxicity exists in these two watersheds, and that it is due to presence of diazinon and chlorpyrifos. There are other pollutants in the watershed and they may create aquatic toxicity as well; however, the preponderance of the toxicity is from diazinon and chlorpyrifos.

The draft TMDL cites surveys and other data that document the use of diazinon and chlorpyrifos in the two watersheds by landuse and other paramaters. I have used similar data in my research. It is a useful way of showing the mass burden of a watershed for specific compounds.

Fortunately, reductions of diazinon and chlorpyrifos will occur because of its withdrawal from the market for use. The Lee et al report documents this withdrawal and projects a decline in usage by 75%. This is good news, but I caution against any speculation that this may eliminate the need for a TMDL. There is no way of accurately predicting, at least at this time with available data, just how long it will take for diazinon and chlorpyrifos concentrations to decline. We still find significant concentrations of DDT and other banned pesticides, even though they have not been used in quite some time. It might be possible to study the potential decline in concentrations and speculate with bounded uncertainty about the expected decline. This might be a useful future study. I believe a TMDL is still necessary.

The draft TMDL identifies the beneficial uses of San Diego Creek and Upper Newport Bay. These include uses that may not be very sensitive to diazinon and chlorpyrifos, such as non-contact recreation, but also uses that can be strongly impacted by aquatic toxicity (e.g. habitat and spawning, reproduction and development). These uses justify the requirements for a TMDL.

Lee et al. note that bioaccumulation of the two pesticides does not occur and other data in the draft TMDL support their assertions. They also speculate that a TMDL could be created around the expected food consumption of harvested fish. This would not be an appropriate method for establishing a TMDL, since the limits would not be protective of the other beneficial uses, noted above.

The draft TMDL in Chapter 3 develops numerical water quality objectives. This is necessary because California and the US EPA have not created numerical concentration standards. I have reviewed the procedures for establishing the values, specifically, those in Table 3-1. They are based upon the California Department of Fish and Game's analysis (Water Quality Criteria for Diazinon and Chlorpyrifos, Administrative Report 00-3, 2000, Office of Spill Prevention and Response). The authors of this report complied all know toxicity studies for diazinon and chlorpyrifos and compared them to the criteria presented in US EPA Report Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses, by Stephan, et al. (1985). I believe the values shown in Table 3-1 are consistent with this procedure and represent a scientifically valid method, consistent with US EPA procedures, for establishing numerical targets.

Response: Comments noted. We agree that monitoring to assess the efficacy of implementation of the TMDL and BMPs will be necessary. Where

existing BMPs are not shown to be effective, revised/new BMPs will need to be implemented. Comments about need/recommendations for additional studies are noted.